PB86-166030

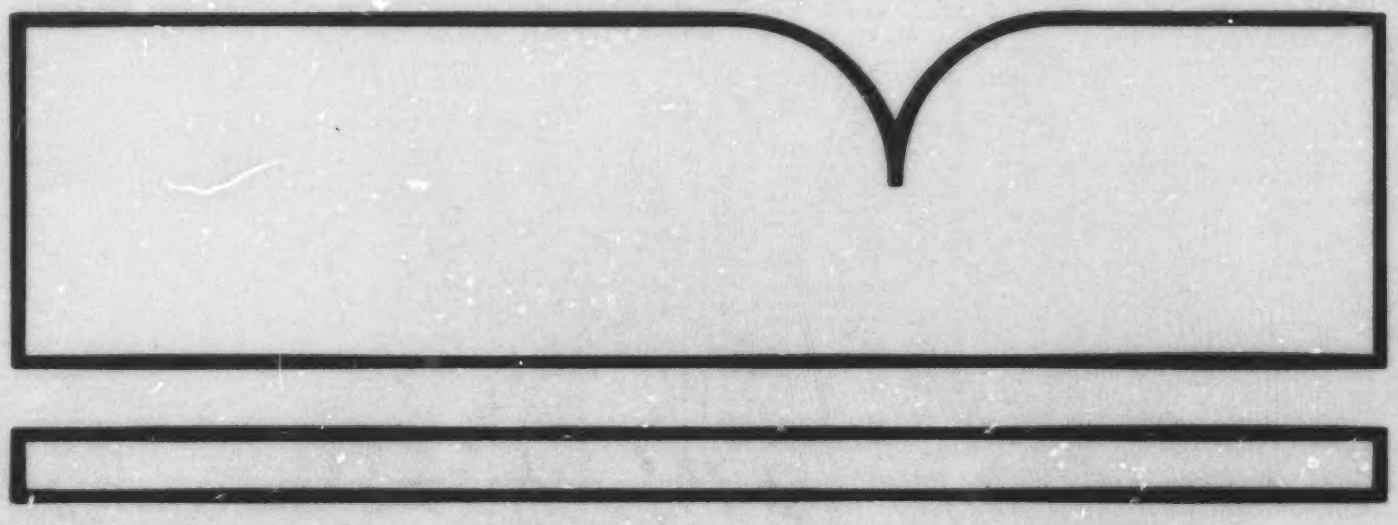
Groundwater Mass Transport and Equilibrium Chemistry Model for Multicomponent Systems

Stanford Univ., CA

Prepared for

Robert S. Kerr Environmental Research Lab.
Ada, OK

1985



U.S. Department of Commerce
National Technical Information Service
NTIS

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. R PB86-166030
EPA/600/J-85/292		

4. TITLE AND SUBTITLE	5. REPORT DATE
A GROUNDWATER MASS TRANSPORT AND EQUILIBRIUM CHEMISTRY MODEL FOR MULTICOMPONENT SYSTEMS (Journal Version)	1985
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Gail A. Cederbert, Robert L. Street, and James O. Leckie	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Civil Engineering Stanford University Stanford, CA 94305	10. PROGRAM ELEMENT NO. CBWD1A
	11. CONTRACT/GRANT NO. CR-808851
12. SPONSORING AGENCY NAME AND ADDRESS Robert S. Kerr Environmental Research Lab. - Ada, OK Office of Research and Development U.S. Environmental Protection AGency Ada, OK 74820	13. TYPE OF REPORT AND PERIOD COVERED
	14. SPONSORING AGENCY CODE EPA/600/15

15. SUPPLEMENTARY NOTES

Published in WATER RESOURCES RESEARCH, 21(8):1095-1104, August 1985.

16. ABSTRACT

A mass transport model, TRANQL, for a multicomponent solution system has been developed. The equilibrium interaction chemistry is posed independently of the mass transport equations which leads to a set of algebraic equations for the chemistry coupled to a set of differential equations for the mass transport. Significant equilibrium chemical reactions such as complexation, ion exchange, competitive adsorption, and dissociation of water may be included in TRANQL. Here, a finite element solution is presented first for cadmium, chloride, and bromide transport in a one-dimensional column where complexation and sorption are considered. Second, binary and ternary ion exchange are modeled and compared to the results of other investigators. Results show TRANQL to be a versatile multicomponent transport model, with potential for extension to a wide range of equilibrium reactions.

p 1095

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
RELEASE TO PUBLIC	UNCLASSIFIED	12
	20. SECURITY CLASS *(This page)*	22. PRICE
	UNCLASSIFIED	

EPA Form 2220-1 (9-73)

WATER RESOURCES RESEARCH, VOL. 21, NO. 8, PAGES 1095–1104, AUGUST 1985

EPA/600/J-85/292
JOURNAL ARTICLE

A Groundwater Mass Transport and Equilibrium Chemistry Model for Multicomponent Systems

GAIL A. CEDERBERG,[1] ROBERT L. STREET, AND JAMES O. LECKIE

Environmental and Water Studies, Department of Civil Engineering, Stanford University, Stanford, California

A mass transport model, TRANQL, for a multicomponent solution system has been developed. The equilibrium interaction chemistry is posed independently of the mass transport equations which leads to a set of algebraic equations for the chemistry coupled to a set of differential equations for the mass transport. Significant equilibrium chemical reactions such as complexation, ion exchange, competitive adsorption, and dissociation of water may be included in TRANQL. Here, a finite element solution is presented first for cadmium, chloride, and bromide transport in a one-dimensional column where complexation and sorption are considered. Second, binary and ternary ion exchange are modeled and compared to the results of other investigators. Results show TRANQL to be a versatile multicomponent transport model, with potential for extension to a wide range of equilibrium reactions.

INTRODUCTION

Modeling the transport of contaminants through groundwater flow systems plays a critical role in any hazardous waste management and disposal program. In the process of understanding such transport many geochemical transport models have been developed [*Rubin and James*, 1973; *Valocchi et al.*, 1981; *Charbeneau*, 1981]. Until recently only a single specific chemical reaction such as ion-exchange or sorption for a small number of reacting solutes has been incorporated into mass transport models. It has also been assumed that the solutes being modeled act independently of the bulk solution composition. Because most contamination sources are actually multicomponent solutions, the need exists for models which are able to incorporate all the significant chemical interactions and processes which affect transport in any given groundwater system. In order to more fully describe and predict the transport of a multicomponent solution in a groundwater system, a general numerical model, TRANQL, was developed and tested.

Several investigators have recently addressed the problem of modeling the transport of a multicomponent solution in equilibrium with a groundwater system. *Rubin* [1983] provides an overall context showing how the nature of the mathematical formulation depends upon the nature of the chemical reactions. *Jennings et al.* [1982], in their work on the groundwater transport of a multicomponent solution composed of metals and ligands, suggest that there are two distinct techniques for modeling multicomponent solutions. The first technique is to insert all of the interaction chemistry directly into the transport equations and to reduce the problem to one strongly nonlinear equation set. The second technique is to pose the equilibrium interaction chemistry independently of the mass transport equations, leading to a set of algebraic equations for the chemistry coupled to a set of differential equations for the mass transport.

Jennings et al. [1982], *Rubin and James* [1973], and *Valocchi et al.* [1981] all follow the first approach. *Jennings et al.* [1982] presented a finite element solution to the modeling of the groundwater transport of a multicomponent solution of metal and ligands for an arbitrary number of components. The chemical reactions they included were soluble complexation and competitive sorption among chemical species. Their model required the phase exchange reactions (i.e., sorption isotherms) to be known explicitly and be differentiable. The *p*H was also considered constant throughout the system. *Rubin and James* [1973] and *Valocchi et al.* [1981] presented finite element solution models for describing the transport of equilibrium-controlled ion exchanging solutes. Both considered binary and multicomponent ion exchange in solution with constant *p*H.

In this first technique where the interaction chemistry is inserted directly into the transport equations, iteration on the entire equation set is required within each time step because the equation system is nonlinear. During the iteration procedure the finite element coefficient matrices must be updated and regenerated at each iteration. Although this method can lead to accurate results by way of a conceptually satisfying algorithm, the method appears to be expensive except for a small number of solutes.

The principal objective of our paper is the presentation of a general transport model using the second technique, together with a demonstration of its applicability and versatility. In the multisolute problem the algebraic equation set for the equilibrium interaction chemistry will contain all of the phase exchange and/or mass action equations necessary to describe significant chemical processes affecting transport such as sorption, complexation, dissociation of water, ion exchange, etc. It is not necessary to assume that the solutes being modeled act independently of the bulk solution composition. The resulting model comprised of the differential and algebraic equation sets may be solved by either iterating between the two equation sets or by combining the two equation sets into one system of equations. In TRANQL a solution is found by iterating between the two equation sets.

The technique of separating the algebraic equation set for the equilibrium chemistry from the differential equation set for the mass transport has been used with some success [*Grove and Wood*, 1979; *Schulz and Reardon*, 1983]. *Grove and Wood* [1979] coupled mineral dissolution and precipitation and ion exchange for three reactive solutes to a one-dimensional transport model which neglected transverse dispersion. The alge-

[1] Now at Los Alamos National Laboratory, Los Alamos, New Mexico.

Copyright 1985 by the American Geophysical Union

Paper number 5W0254.
0043-1397/85/005W-0254$05.00

NTIS is authorized to reproduce and sell this report. Permission for further reproduction must be obtained from the copyright owner.

braic equation set for the chemistry and the differential equation set for the mass transport were solved sequentially, rather than simultaneously. The differential equation set was solved using a finite-difference technique centered in space and time. *Schulz and Reardon* [1983] presented a combined two-dimensional mixing cell–analytical solution model which described multiple reactive solute transport in unidirectional groundwater flow regimes. The chemical equilibria for four solutes undergoing ion exchange and mineral precipitation and dissolution was calculated using a mixing cell model. The mixing cell model was coupled to and solved sequentially with an analytical transport model. This model is limited in its application to groundwater sites containing one-dimensional flow, although both transverse and longitudinal dispersion were considered.

Miller and Benson [1983] modeled one-dimensional transport in a saturated porous medium. They combined the differential equation set for the mass transport and the algebraic equation set for the chemistry into one differential-algebraic system of equations. The chemical reactions in their model included sorption of ions and complexes in the solid phase, formation of complexes in the aqueous phase, and dissociation of water. A Newton-Raphson iteration technique was used to solve the system of equations. Because the system of equations was solved for chemical concentrations along previously generated streamlines, transverse dispersion was ignored.

Posing the chemical equilibria equations and the transport equations independently and iterating between the two offers some advantages over inserting all the chemical equations into the transport equations. If the finite element method is used in solving the differential equations, as in the work of *Jennings et al.* [1982] and *Valocchi et al.* [1981], reformulation of the finite element matrices within each time step is not required. The phase exchange relations (i.e., sorption isotherms) need not be known explicitly or be differentiable because the equilibrium chemistry is posed as a set of algebraic equations.

In the sections that follow we first present the model formulation and the solution procedure. Two example applications follow. The first examines the transport of a heavy metal, cadmium, in the presence of complexing ligands, chloride, and bromide. The second examines the application of TRANQL to a system of ion exchanging solutes. From these examples we conclude that TRANQL appears to be a versatile and general multicomponent transport model. TRANQL offers a framework for incorporation of all of the necessary chemical reactions and models to describe the transport of any particular set of solutes.

Model Formulation for Cadmium Transport

TRANQL was initially used to investigate the geochemical transport of cadmium in a multicomponent solution. Hence to give specificity to the discussion, the details of TRANQL's structure and solution scheme are presented in the context of cadmium transport in a multicomponent solution containing chloride and bromide. The general concepts are easily extended to other multicomponent systems. Dispersion, advection, complexation in the aqueous phase, and sorption of free cadmium are the physical and chemical processes considered. Also, while the concepts are valid in three-dimensional flow, the development is carried out here for one-dimensional flow, and the examples given are for one-dimensional and for radial flows.

The nomenclature and definitions used in the development follow those of *Westall* [1979]. A species is defined as every chemical entity to be considered in the transport problem. The species ($c_1, c_2, \cdots, c_n$) are not limited to those in the aqueous phase but also include those reacted with the porous medium. Associated with each entity in the group of species is a mass law equation and an equilibrium stability constant. A set of components ($T_1, T_2, \cdots, T_m$) is defined so that for each species an equation can be written expressing each entity as the product of a reaction involving only components, and no component can be written as the product of a reaction involving other components. This definition is similar to Gibb's definition of components [*Gibbs*, 1957]. In algebraic terms, components can be described as a linearly independent set spanning the species space. Once the set of components is defined, the representation of the species in terms of this set of components is unique. These definitions of species and components allow us to pose the interaction equilibrium chemistry equations independently of the mass transport equations.

Two models of ion sorption presently used are the surface complexation model and the constant charge model. The surface complexation model includes surface ionization and complexation at the solid-water interface and provides a more realistic treatment of sorbing substrates whose surface charge is not constant but a function of *p*H. Surface complexation models can be further broken down into several submodels. Two surface complexation models are the constant capacitance model and the triple-layer model. Both of these surface complexation models, which also allow for the simultaneous sorption of cations and anions, have been used successfully to model ion sorption on oxide surfaces in laboratory experiments [*Stumm et al.*, 1976; *Davis et al.*, 1978; *Davis and Leckie*, 1978, 1980]. The constant charge model was used successfully by *Valocchi et al.* [1981] to model the transport of ion exchanging solutes in groundwater.

In the constant charge model it is assumed that a fixed-charge imbalance exists on the surface of the sorbing substrate. This fixed-charge imbalance restricts the use of the constant-charge model to systems undergoing little or no change in *p*H. The constant-charge model must also deal with anions and cations separately. In the examples given in this paper the sorption of cadmium was modeled using the constant capacitance surface complexation model, whereas ion exchange was modeled using the constant charge model. Both models were easily incorporated into TRANQL.

The chemical species considered in this development of cadmium transport are listed in Table 1 along with mass law equations and stability coefficients. As seen from this list the species are written as the product of one or more components. Species 14 represents the concentration of free cadmium sorbed onto the solid surface. A range of values is given for the stability coefficient of sorbed cadmium. The range is representative of cadmium sorption stability coefficients for pseudooxide sorption substrates and the solute concentrations used in the simulations.

Generally, a sorption stability coefficient is a strong function of many system parameters such as *p*H, surface site density, and composition of porous medium. The sorption stability coefficient may vary over orders of magnitude, depending upon these parameter values. Therefore the sorption equilibrium coefficients should be determined for each multicomponent–porous medium system under consideration. The values of these coefficients should remain constant in the face of perturbations in fluid composition as long as the surface characteristics remain constant. The range of stability constants for cadmium sorption is used to test the sensitivity of

TABLE 1. Reactions and Mass Law Equations: Cadmium Transport

Reaction	Species	$Log_{10}K$	Mass Law Equation					
1	$H^+ = H^+$	0					$[H^+]$	$K_1 = [H^+]$
2	$Cd^{2+} = Cd^{2+}$	0			$[Cd^{2+}]$			$K_2 = [Cd^{2+}]$
3	$Cl^- = Cl^-$	0	$[Cl^-]$					$K_3 = [Cl^-]$
4	$Br^- = Br^-$	0		$[Br^-]$				$K_4 = [Br^-]$
			Complexation					
5	$Cd^{2+} + Cl^- = CdCl^+$	1.8	$[Cl^-]$		$[Cd^{2+}]$			$K_5 = [CdCl^+]$
6	$Cd^{2+} + 2Cl^- = CdCl_2$	2.6	$[Cl^-]^2$		$[Cd^{2+}]$			$K_6 = [CdCl_2]$
7	$Cd^{2+} + Br^- = CdBr^+$	2.2		$[Br^-]$	$[Cd^{2+}]$			$K_7 = [CdBr^+]$
8	$Cd^{2+} + 2Br^- = CdBr_2$	3.0		$[Br^-]^2$	$[Cd^{2+}]$			$K_8 = [CdBr_2]$
9	$Cd^{2+} - H^+ + H_2O = CdOH^+$	−12.69			$[Cd^{2+}]$		$[H^+]^{-1}$	$K_9 = [CdOH^+]$
			Dissociation of Water					
10	$-H^+ + H_2O = OH^-$	−13.91					$[H^+]^{-1}$	$K_{10} = [OH^-]$
			Sorption					
11	$SOH = SOH$	0				$[SOH]$		$K_{11} = [SOH]$
12	$SOH + H^+ = SOH_2^+$	7.4				$[SOH]$ $[e^{-F\psi/RT}]$	$[H^+]$	$K_{12} = [SOH_2^+]$
13	$SOH - H^+ = SO^-$	−9.24				$[SOH]$ $[e^{-F\psi/RT}]$	$[H^+]^{-1}$	$K_{13} = [SO^-]$
14	$SOH - H^+ + Cd^2 = SOCd^+$	−7→−11			$[Cd^{2+}]$	$[SOH]$ $[e^{-F\psi/RT}]$	$[H^+]^{-1}$	$K_{14} = [SOCd^+]$

TRANQL to changes in chemical parameter values. The list of components which make up the species is given in Table 2, which also contains the material balance equation for each component. The total analytical concentration of each component is the sum of the concentration of the species in which that component occurs either alone or in association with other components. Table 3 presents the reactions listed in Table 1 in a tabular format. The numbers in the table are the stoichiometric coefficients for a given component in the formation of the species. The sorption process is represented by protonation-deprotonation reactions at amphoteric surfaces (species 12 and 13) where SOH represents a surface hydroxyl group. Surface hydrolysis is formulated using the constant capacitance (Helmholtz) model where the media surface is at potential ψ with respect to the bulk of solution. Because of the potential ψ, the exponential of the electrostatic interaction energy, $e^{-F\psi/RT}$, must be accounted for in the mass action laws of reactions 12, 13, and 14 and is included in the set of components. Further details of the surface complexation model can be found in the literature [*Hohl and Stumm*, 1976; *Westall and Hohl*, 1980].

As chemical equilibrium problems are normally posed, the equilibrium concentrations of the species are to be found, given the total (analytical) concentrations of all components and the stoichiometry and stability constants of the species. A computer code, MICROQL, was developed to solve such a chemical equilibrium problem [*Westall*, 1979]. MICROQL is a scaled-down version of the comprehensive chemical equilibrium computer code, MINEQL [*Westall et al.*, 1976], and includes the surface complexation model described above. The solution procedure is well documented [*Westall*, 1979], so only a general outline of the procedure is given here.

MICROQL uses the mass law equations and stability constants for the species and the material balance equations for each component to define the chemical equilibrium problem. From an initial guess of the free concentrations of components, the provisional concentrations of the species are computed. The free concentration of a component is defined as the concentration of that component found as a single entity (noncomplexed) in the aqueous phase. From the provisional concentrations of the species, the error (the remainders in the material balance equations) is computed. Then, an iterative technique is used to find improved values of the free concentrations of components such that the values of the remainders approach a prescribed lower limit. The improved values are found by use of the Newton-Raphson method. Depending upon the values of the initial guesses, the number of components, and the number of species in the system, the number of iterations to reach convergence will vary. Typically, the number of iterations required to reduce the error to 10^{-5} rarely exceeds 5. In TRANQL, MICROQL is used to fully describe all chemical processes, while the general mass transport equations are used to describe advective-dispersive transport of the chemical species.

TABLE 2. Component Material Balance Equations

Component	Material Balance Equation
$T_1 = Cl_T$	$= [Cl^-] + [CdCl^+] + 2[CdCl_2]$
$T_2 = Br_T$	$= [Br^-] + [CdBr^+] + 2[CdBr_2]$
$T_3 = Cd_T$	$= [Cd^{2+}] + [CdCl^+] + [CdCl_2] + [CdBr^+] + [CdBr_2] + [CdOH^+] + [SOCd^+]$
$T_4 = SOH_T$	$= [SOH] + [SOH_2^+] + [SO^-] + [SOCd^+]$
$T_5 = T_{\sigma T}$	$= [SOH_2^+] - [SO^-] + [SOCd^+]$
$T_6 = H_T$	$= [H^+] + 2[SOH_2^+] - [CdOH^+] - [OH^-] - [SO^-] - [SOCd^+]$

T_σ represents the charge on the surface, defined as the excess of positive groups over negative groups.

TABLE 3. Stoichiometry of Reactions

		Components					
Reaction	Species	Cl^-	Br^-	Cd^{2+}	SOH	$e^{-F\psi/RT}$	H^+
1	H^+	0	0	0	0	0	1
2	Cd^{2+}	0	0	1	0	0	0
3	Cl^-	1	0	0	0	0	0
4	Br^-	0	1	0	0	0	0
5	$CdCl^+$	1	0	1	0	0	0
6	$CdCl_2$	2	0	1	0	0	0
7	$CdBr^+$	0	1	1	0	0	0
8	$CdBr_2$	0	2	1	0	0	0
9	$CdOH^+$	0	0	1	0	0	−1
10	OH^-	0	0	0	0	0	−1
11	SOH	0	0	0	1	0	0
12	SOH_2^+	0	0	0	1	1	1
13	SO^-	0	0	0	1	−1	−1
14	$SOCd^+$	0	0	1	1	−1	−1

The basic equations describing the mass transport of reacting species have been presented by several investigators [*Bear*, 1971; *Freeze and Cherry*, 1979]. For one-dimensional flow in a homogeneous, isotropic porous medium, the equations for reacting species can be expressed as

$$\frac{\partial c_i}{\partial t} + \frac{\rho}{\theta}\frac{\partial \bar{c}_i}{\partial t} = D_L \frac{\partial^2 c_i}{\partial x^2} - v\frac{\partial c_i}{\partial x} + S_{c_i} \qquad (1)$$

$$i = 1, 2, \cdots, n_{aq}$$

where

- c_i aqueous phase concentration of species i (moles/L);
- $\bar{c}_i$ sorbed phase concentration of species i (moles/g);
- n_{aq} number of aqueous species to be considered (= 13 here, for example);
- S_{c_i} source-sink term for species i due to aqueous phase complexation;
- θ medium porosity;
- ρ bulk density of medium (g/L);
- D_L coefficient of hydrodynamic dispersion (m^2/hour);
- v average pore velocity (m/hour);
- t time (hour);
- x distance (m).

For a nonsorbing species the second term on the left-hand side of (1) is zero. The third term on the right-hand side of (1) represents the amount of species i lost or gained due to aqueous phase complexation. This term is a complex function of the concentrations of all components in the system. To solve these equations appropriate initial and boundary conditions must be imposed and the sorbed phase of concentration i must be defined. In a multispecies solution where the sorbed phase concentration of species i is a function of the concentration of the other aqueous species concentrations, a nonlinear system of coupled solute transport equations such as those of *Jennings et al.* [1982] arises. By making use of the definitions for species and components, the set of n_{aq} mass transport equations for the species can be reduced to a set of mass transport equations for the components. The number of transport equations reduces to the number of components which are not time invariant.

For the sake of simplicity, in this development it is assumed that component T_6, i.e., the *p*H, is constant, although this is not a necessary restriction. The total number of sorption sites, T_5, is also considered to be constant. If the reactions are *p*H dependent, the number of sites participating in sorption could change. Finally, the electrostatic potential component, T_4, is used only in MICROQL and does not enter into the mass transport equations.

As can be seen from Table 2 the total concentration of chloride, T_1, is equal to the sum of the concentrations of chloride in species 3, 5, and 6. Adding the mass transport equations for species 3, 5, and 6 yields the following equation:

$$\frac{\partial}{\partial t}([Cl^-]) + \frac{\partial}{\partial t}([CdCl^+]) + \frac{\partial}{\partial t}(2[CdCl_2])$$

$$= L[Cl^-]) + L([CdCl^+]) + L(2[CdCl_2]) \qquad (2)$$

where $L = (D_L\ \partial^2/\partial x^2 - v\partial/\partial x)$. The source-sink terms of (2) have been incorporated into the terms on the left-hand side of (2). Adding the terms gives

$$\frac{\partial}{\partial t}(Cl_T) = L(Cl_T) \qquad (3)$$

where Cl_T = total Cl^- concentration (moles/liter). Because Cl^- is a conservative (nonreacting) component, the total Cl^- concentration, Cl_T, equals the total aqueous concentration of Cl^-, Cl_{AQ}, i.e., $Cl_{AQ} = Cl_T$. Equation (3) is the familiar conservative transport equation. Here, three mass transport equations for a set of species have been reduced to one equation for a component. A similar analysis can be supplied for component T_2, Br^-. The resulting equation is

$$\frac{\partial}{\partial t}(Br_T) = L(Br_T) \qquad (4)$$

where Br_T equals the total concentration of Br^- in the system, i.e., the sum of the concentrations of Br^- in species 4, 7, and 8.

The final component to be considered is T_3, Cd_T. The total concentration of cadmium, Cd_T, is equal to the sum of the concentrations of Cd^{2+} in species 2, 5, 6, 7, 8, 9, and 14. When the set of mass transport equations for cadmium is summed we have

$$\frac{\partial}{\partial t}([Cd^{2+}] + [CdCl^+] + [CdCl_2] + [CdBr^+] + [CdBr_2]$$

$$+ [CdOH^+]) - \frac{\partial}{\partial t}\left(\frac{\rho}{\theta}[SOCd^+]\right)$$

$$= L([Cd^{2+}] + [CdCl^+] + [CdCl_2] + [CdBr^+]$$

$$+ [CdBr_2] + [CdOH^+]) \qquad (5)$$

Equation (5) can be rewritten in the following form:

$$\frac{\partial}{\partial t}(Cd_{AQ}) - \frac{\partial}{\partial t}\left(\frac{\rho}{\theta}[SOCd^+]\right) = L(Cd_{AQ}) \qquad (6)$$

where Cd_{AQ} is the total concentration of cadmium in the aqueous phase and, in consistent units, (ρ/θ) $[SOCd^+]$ is the total concentration of sorbed cadmium. The transport of components Cl_T and Br_T are modeled using the total concentration of each component. The transport of cadmium can be formulated in a similar manner even though it is a nonconservative component. Rewriting equation (6) in the following form is the key:

$$\frac{\partial}{\partial t}(Cd_T) = L(Cd_{AQ}) \qquad (7)$$

where $Cd_T = Cd_{AQ} + (\rho/\theta)$ $[SOCd^+]$ represents the total concentration of cadmium in the system. The time derivitive of the total cadmium concentration is now a function only of the transport by advection and dispersion of the total aqueous cadmium concentration. In general, then, in a system with more than one component that reacts with the solid matrix, the transport of those components can be modeled using equations similar to (7). The total aqueous concentration required in (7) is determined by using MICROQL. Thus joining MICROQL with a transport model, in our case the ISOQUAD code (G. F. Pinder, unpublished manuscript, 1976), and provides the basis for our transport plus equilibrium chemistry, or TRANQL, code.

The set of transport equations for the species which originally numbered 13 has now been reduced to a set of three partial differential equations, one for each component which is not time invariant. Instead of formulating the transport equations around the mass balance for each species in the aqueous phase, (3), (4), and (7) represent mass balance equations for the total concentration of each component. This formulation

allows the interaction chemistry to be posed independently of the mass transport equations and coupling of the two sets in a precise manner. When the equations for the species are summed into one equation for a component, the source-sink terms in (1) become a part of the mass balance for Cd_T. The component equations are coupled in the sense that concentrations of Cd_{AQ} and $[SOCd^+]$ are functions of the concentrations of the conservative components (here, Cl_T and Br_T).

Solution Procedure

The development of TRANQL described above does not place any restrictions on boundary conditions. For the work presented here all equations have been solved on a finite domain of length L_T with Dirichlet boundary conditions. Equilibrium initial conditions must be specified in the system. The initial and boundary conditions corresponding to step function inputs at the boundary $x = 0$ are stated as

$$\begin{aligned} T_i(x, 0) &= T_{in} \qquad x > 0 \\ T_i(0, t) &= T_{if} \qquad t > 0 \qquad i = 1, 2, 3 \\ T_i(L_T, t) &= T_{in} \qquad t > 0 \end{aligned} \tag{8}$$

where T_{if} is the concentration of component i in the feed or input solution, and T_{in} is the concentration of component i in the initial or native solution.

The numerical technique used for solving (3), (4), and (7), subject to the given initial and boundary conditions, is the Galerkin finite element method with a centered approximation of the time derivative. Because the numerical formulation of the conservative (i.e, Cl_T and Br_T) and the nonconservative (i.e, Cd_T) transport equations take different forms, the finite element formulations are presented. Details of the finite element method formulation can be found in the literature [*Pinder and Gray*, 1977]. The computer code is an adaption of ISOQUAD (G. F. Pinder, unpublished manuscript, 1976). The advective, dispersive, conservative mass transport equations for Cl_T and Br_T are approximated by the finite element method to matrix equations of the form

$$\mathbf{N}\frac{d}{dt}\{T_T\}_i + \mathbf{P}\{T_T\}_i = \mathbf{f} \qquad i = 1, 2 \tag{9}$$

where $\mathbf{N}$ and $\mathbf{P}$ denote coefficient matrices containing the contributions to transport from advection and dispersion, $\{T_T\}_i$ denotes a vector of the unknown nodal coefficients representing the total concentrations of the aqueous conservative components (here $\{T_T\}_1 = \{Cl_T\}$ and $\{T_T\}_2 = \{Br_T\}$), and $\mathbf{f}$ is a vector of constants containing the contribution from boundary conditions. By introducing a finite difference approximation of the time derivative centered at $t + \Delta t/2$ and by using

$$\{T_T\}_i^{t+\Delta t} = 2\{T_T\}_i^{t+\Delta t/2} - \{T_T\}_i^t + 0(\Delta t^2) \qquad i = 1,2 \tag{10}$$

to convert the problem to one for the unknowns $\{T_T\}_i^{t+\Delta t/2}$ one changes (9) into a set of algebraic equations. The result is an implicit formulation, which while not second-order accurate in time, possesses a time truncation error which is about one quarter of the first-order error in the explicit Euler scheme. The difference equation is

$$\left(\frac{2}{\Delta t}\mathbf{N} + \mathbf{P}\right)\{T_T\}_i^{t+\Delta t/2} = \mathbf{f} - \frac{2}{\Delta t}\mathbf{N}\{T_T\}_i^t \qquad i = 1, 2 \tag{11}$$

This system of linear equations is solved using Gauss elimination to obtain the solution $\{T_T\}^{t+\Delta t/2}$. Then, the solution at the new time, $t + \Delta t$, is given by (10). The concentration of each conservative component is determined in this manner.

The matrix equation formulation for cadmium transport takes the form

$$\mathbf{N}\frac{d}{dt}\{Cd_T\} + \mathbf{P}\{Cd_{AQ}\} = \mathbf{f} \tag{12}$$

where $\{Cd_T\}$ denotes a vector of the unknown nodal coefficients representing the total concentration of cadmium, and $\{Cd_{AQ}\}$ denotes a vector representing the total aqueous cadmium concentration. The above implicit formulation now yields

$$\frac{2}{\Delta t}\mathbf{N}\{Cd_T\}^{t+\Delta t/2} = \mathbf{f} + \frac{2}{\Delta t}\mathbf{N}\{Cd_T\}^t - \mathbf{P}\{Cd_{AQ}\}^{t+\Delta t/2} \tag{13}$$

The time derivative of total cadmium concentration at the intermediate time step is a function of the total aqueous cadmium concentration at the intermediate time step. To solve for the cadmium concentration, iteration between MICROQL and (13) is necessary. However, within each iteration the coefficient matrices, which do not depend on the unknowns need not be regenerated. Finally, the solution at the new time, $t + \Delta t$, is

$$\{Cd_T\}^{t+\Delta t} = 2\{Cd_T\}^{t+\Delta t/2} - \{Cd_T\}^t \tag{14}$$

Equations (10), (11), (13), and (14) combined with MICROQL constitute the basis of TRANQL.

In general, at each time step, the following procedure is implemented to obtain a solution.

1. Use MICROQL to initialize the system to equilibrium conditions.
2. Calculate the solutions $\{Cl_T\}$ and $\{Br_T\}$ to (11) and (10), respectively, (the mass transport equations for the conservative components) at new time step $(t + \Delta t/2)$ and advanced time step $(t + \Delta t)$.
3. Use MICROQL to compute an estimate of $\{Cd_{AQ}\}^*$ and $\{SOCd^+\}^*$ at $(t + \Delta t/2)$ using new values of $\{Cl_T\}$ and $\{Br_T\}$ at $(t + \Delta t/2)$ and old values of $\{Cd_T\}$. The tolerance level in MICROQL was set at 10^{-5}.
4. Compute a provisional solution, $\{Cd_T\}^*$, to (13) using $\{Cd_{AQ}\}^*$ from step 3.
5. Given this provisional solution of (13), $\{Cd_T\}^*$, use MICROQL to compute a new estimate of $\{Cd_{AQ}\}^{**}$ and $\{SOCd^+\}^{**}$.
6. Compute a new provisional solution of (13), $\{Cd_T\}^{**}$, using the results of step 5.
7. Repeat steps 5 and 6 until some prescribed convergence tolerance, δ, is met for $\{Cd_T\}$ at $(t + \Delta t/2)$ $[|Cd_T^{**} - Cd_T^*|/Cd_T^{**} = \delta]$. A $\delta = 10^{-5}$ was used for this work.
8. Compute new values of $\{Cd_T\}$ at the advance time level $(t + \Delta t)$ using (14).

Cadmium Transport Simulation

The transport of a multicomponent solution of cadmium, chloride, and bromide in a one-dimensional laboratory column was simulated to investigate the behavior of TRANQL. The species and components of the equilibrium chemical system were described above and listed in Tables 1, 2, and 3. The physical and chemical processes considered include dispersion, advection, formation of complexes in the

TABLE 4. Parameters of Simulated Column Experiment

Parameter	Value
Physical	
L_T, length of column	10 cm
θ, porosity	0.3
v, average pore velocity	8 cm/day
D_L, longitudinal dispersion coefficient	0.16 cm^2/day
ρ, bulk density of medium	2500 g/L
Chemical Sorption	
T_s, total number of sites	0.046 moles/L
I, ionic strength	0.1 moles/L
pH, held constant	7.0
C_1, capacitance	1.06 F/m^2
a, solid surface area	1.0 m^2/gm

TABLE 5. Concentration of Components for Test Cases: Initial and Boundary Conditions

Case	Components Cd_T	Cl_T	Br_T	Conditions	
	Group 1: Background Levels of Cl^- and Br^- (M)				
1	0.00001	0.0003	0.0001	$0 < x < \infty$	$t = 0$
	0.0001	0.0003	0.0001	$x = 0$	$t \geq 0$
2	0.0001	0.0003	0.0001	$0 < x < \infty$	$t = 0$
	0.0001	0.003	0.001	$x = 0$	$t \geq 0$
3	0.00001	0.0003	0.0001	$0 < x < \infty$	$t = 0$
	0.0001	0.003	0.001	$x = 0$	$t \geq 0$
	Group 2: Higher Than Background Levels of Cl^- and Br^- (M)				
4	0.00001	0.003	0.001	$0 < x < \infty$	$t = 0$
	0.0001	0.003	0.001	$x = 0$	$t \geq 0$
5	0.0001	0.003	0.001	$0 < x < \infty$	$t = 0$
	0.0001	0.03	0.01	$x = 0$	$t \geq 0$
6	0.00001	0.003	0.001	$0 < x < \infty$	$t = 0$
	0.0001	0.03	0.01	$x = 0$	$t \geq 0$

$Br_T = Cl_T/3$ is assumed for these illustrations.

aqueous phase, and sorption of free cadmium. The pH of the system was considered to be constant. Transport parameters and coefficients used in the simulations are typical of those used in column experiments and have been taken from the literature [*Lindstrom and Boersman*, 1973; *Anderson*, 1979]. The parameters and coefficients selected are listed in Table 4.

As was previously stated, the sorption of cadmium is expected to be a function of the concentrations of the complexing ligands in solution and the composition of the sorption substrate. The variation of the composition of the sorbing substrate in this simulation is reflected in the range of sorption equilibrium stability constants for free cadmium considered in Table 1. To fully investigate the effect of the concentration of complexing ligands and the composition of sorbing substrate on the concentration of aqueous cadmium, six test cases were run for both the upper and lower limit of the sorption stability constant. The six cases were separated into two groups. The first group considered cadmium transport in the presence of Cl_T and Br_T near background concentrations. The second group considered the transport of cadmium in the presence of Cl_T and Br_T above background concentrations. The boundary conditions for each of the principal components (i.e., Cl_T, Br_T, and Cd_T) were combined and varied to yield three test runs for each group. Thus a total of 12 simulations were run for the cadmium transport example.

The initial and boundary conditions for each case within each group are listed in Table 5. For each case the column was in chemical equilibrium at time = 0. Case 1 and 4 correspond to a step input of Cd_T, with Cl_T and Br_T held constant. Case 2 and 5 correspond to a step input of Cl_T and Br_T, with Cd_T being held constant. Case 3 and 6 correspond to a step input of Cl_T, Br_T, and Cd_T. The numerical code was run to simulate operation of the columns for 15 hours of real time.

Figures 1, 2, and 3 show the results of the simulations for each case where the sorption equilibrium constant is at a maximum (i.e., $\log_{10}K_{SOCd^+} = -7.0$). Significant sorption of cadmium is observed for these six examples. When the six cases were run with the sorption equilibrium constant set to a minimum (i.e., $\log_{10}K_{SOCd^+} = -11.0$), the amount of cadmium sorbed throughout the system was less than 0.05%. Therefore the results of those simulations are discussed but not presented graphically.

The six simulations presented in Figures 1, 2, and 3 demonstrate the need for and usefulness of TRANQL. For the simulations the grid spacing was 0.25 cm, the time step was 0.5 hours, and the number of iterations for convergence averaged 4 with the tolerance, δ, set at 0.00001. Although the present scheme is implicit, the selection of time steps and nodal spacing was based on the finite element method criterion of *Meyers* [1978] which is $D\Delta t/(\Delta x)^2 \leq 1/12$ so that possible oscillations in solutions found by this hybrid implicit scheme could be avoided.

Figure 1 shows that with Cl_T and Br_T held constant, sorbed cadmium [$SOCd^+$] decreases and Cd_{AQ} increases as Cl_T and Br_T increase. In Figure 2 it can be seen that [$SOCd^+$] decreases and Cd_{AQ} increases in the column as Cl_T and Br_T increase. The increased concentrations of Cl_T and Br_T cause the cadmium which was initially sorbed onto the porous medium to desorb, complex with Cl^- and Br^-, and enter the aqueous phase. In Figure 3 when the step input of Cl_T, Br_T, and Cd_T is used as a boundary condition, Cd_{AQ} is again increased as Cl_T and Br_T are increased. The value of [$SOCd^+$] is smallest when Cl_T is at a maximum. As Cl_T and Br_T are increased cadmium becomes more mobile and it transported further down the column with respect to the predicted cadmium concentrations when Cl_T and Br_T are at a minimum. As seen from these results the partitioning of Cd is a strong function of the Cl_T concentration. As the concentrations of Cl_T and Br_T were increased for cases 1, 2, and 3, the percent of cadmium sorbed decreased as observed in Figures 1, 2, and 3. As the concentrations of Cl_T and Br_T are increased, Cd_{AQ} is

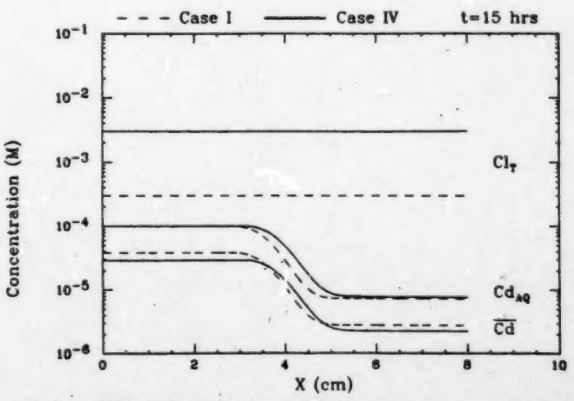


Fig. 1. TRANQL simulations of Cd_{AQ} transport in solution of 3×10^{-4} M Cl_T and 1×10^{-4} M Br_T (case 1) and 3×10^{-3} M Cl_T and 1×10^{-3} M Br_T (case 4).

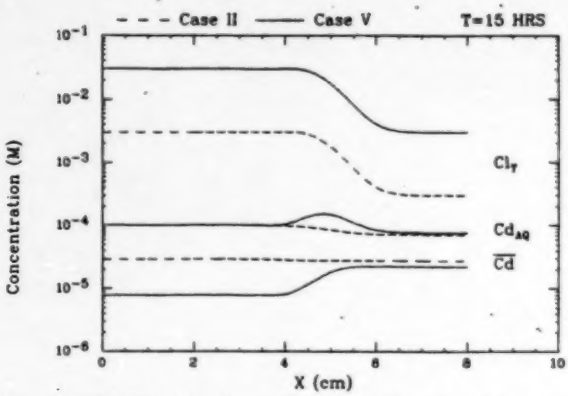


Fig. 2. TRANQL simulations of 3×10^{-3} *M* (case 2) and 3×10^{-2} *M* (case 5) Cl_T transport in solution of 10^{-4} *M* Cd_T.

transported further down the column due to the equilibrium partitioning of cadmium. This behavior is consistent with results obtained in laboratory experiments [*Leckie et al.*, 1980]. The results obtained from the simulations where the sorption equilibrium constant was a minimum are also consistent with other laboratory experiments [*Davis and Leckie*, 1978, 1979]. Finally, *Donner* [1978] and *Donner et al.* [1982] showed from their experimental laboratory column results that chloride has a marked effect on the mobility of cadmium. This effect was found to be directly related to the degree of chlorocomplex formation as predicted from equilibrium stability coefficients. The greater the amount of chloride present, the higher was the observed mobility of cadmium. As in our example, cadmium mobility increased with increasing concentrations of Cl_T.

Two general conclusions can be drawn from these simulations of cadmium transport in a multicomponent solution. First, the partitioning between the sorbed and fluid phases of a particular component (e.g., Cd_T) in a multicomponent solution cannot necessarily be represented in terms of a linear isotherm involving only the aqueous species (here, Cd_{aq}). In these circumstances a typical partition coefficient, K_d, for a species will not be spatially or temporally constant in a flow system and should not be used. The use of single K_d values in transport models will, in cases such as these, lead to erroneous results. Second, the sorption equilibrium constants that result from characterizing the sorbing substrate significantly affect the percent of component (i.e., Cd_T) sorbed. Thus at the risk of restating the obvious, sorption equilibrium constants must be determined for the particular component-porous medium systems under consideration.

Ion Exchange Simulation

Model Formulation and Solution Procedure

Ion exchange is a chemical reaction which has been observed to significantly affect the chemical composition of groundwater systems [*Grove and Wood*, 1979; *Roberts et al.*, 1978, 1982]. Here, binary and ternary homovalent ion exchange are modeled using the constant charge model assuming a constant system *p*H. Because of TRANQL's structure, the ion exchange reactions are easily substituted into the chemical reaction submodel, MICROQL, with no change to the transport equation set. In this section the formulation and inclusion of binary and ternary ion exchange into TRANQL are presented.

The set of mass transport and chemical equilibrium equations used to define the system of ion exchanging solutes is similar to that of *Valocchi et al.* [1981]. In one-dimensional flow the basic transport model for binary homovalent exchange can be expressed as

$$\frac{\partial c_i}{\partial t} + \frac{\rho \partial \bar{c}_i}{\theta \partial t} = L(c_i) \qquad i = 1, 2 \tag{15}$$

$$c_1 + \bar{c}_2 X \rightleftarrows \bar{c}_1 X + c_2 \qquad K_{12} = \bar{c}_1 c_2 / c_1 \bar{c}_2 \tag{16}$$

$$\bar{c}_s = \sum_{i=1}^{2} \bar{c}_i = \bar{c}_1 + \bar{c}_2 \tag{17}$$

$$c_s = \sum_{i=1}^{2} c_i = c_1 + c_2 \tag{18}$$

where

$\bar{c}_s$ cation exchange capacity (CEC) of medium (meq/g);
c_s concentration sum of all pore fluid ions (meq/L);
K_{12} mass action selectivity coefficient;
X negatively charged site on the solid matrix.

Initial and boundary conditions correspond to a step function input at the boundary and are given by (8). Solution-phased activity coefficients have not been included for reasons of developmental simplicity.

If it is assumed that the cation exchange capacity is time invariant, the addition of the two equations represented by (15) for species 1 and 2 yields

$$\partial(c_s)/\partial t = L(c_s) \tag{19}$$

The total number of equivalents of exchangable ions, c_s, satisfies a conservative mass balance as did components Cl_T and Br_T in the cadmium transport example. The original set of unknowns, (c_1, c_2) can be replaced by (c_i, c_s), where i equals either 1 or 2. Letting $i = 1$, we can write (15) in a formulation similar to that for cadmium. The resulting equation for c_1 is

$$\partial(c_{1_T})/\partial t = L(c_1) \tag{20}$$

where $c_{1_T} = c_i + (\rho/\theta)\bar{c}_i = c_{1_{aq}} + (\rho/\theta)\bar{c}_1$.

The transport portion of TRANQL is represented by (19), (20), and (8). The equilibrium ion exchange chemistry is represented in tabular format in Table 6. Table 6 lists the set of chemical species and the set of components considered, their mass and material balance relationships, and the common logarithm of their stability constants. In order to represent an

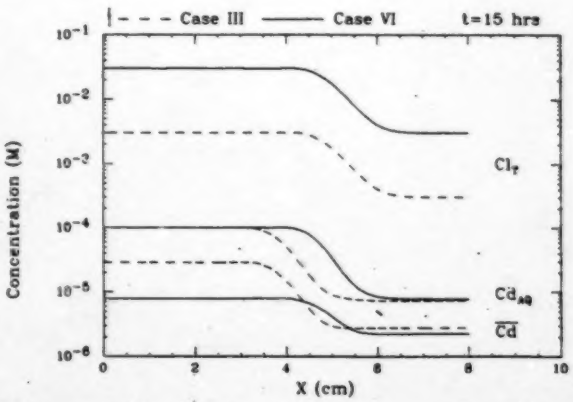


Fig. 3. TRANQL simulations of Cd_{aq} transport and 3×10^{-3} *M* (case 3) and 3×10^{-2} *M* (case 6) Cl_T transport.

TABLE 6. Stoichiometry of Binary Homovalent Ion Exchange Reactions

Species	Components c_1	c_2	$\bar{c}_s$	H^+	$\text{Log}_{10} K$
1 c_1	1	0	0	0	0
2 c_2	0	1	0	0	0
3 $\bar{c}_1$	1	0	1	−1	$\log_{10} K_1$
4 $\bar{c}_2$	0	1	1	−1	$\log_{10} K_2$
5 H^+	0	0	0	1	0

Here $(c_2)_T = c_2 + \bar{c}_2 = (c_s - c_1) + (\bar{c}_s - \bar{c}_1)$.

TABLE 8. Stoichiometry of Palo Alto Baylands Ion Exchange Reactions

Species	Components Na^+	Mg^{2+}	Ca^{2+}	$\bar{c}_s$	H^+	$\log_{10} K$
1 Na^+	1	0	0	0	0	0
2 Mg^{2+}	0	1	0	0	0	0
3 Ca^{2+}	0	0	1	0	0	0
4 $\overline{Na}^+$	1	0	0	1	−1	$\log_{10} K_1$
5 $\overline{Mg}^{2+}$	0	1	0	2	−2	$\log_{10} K_2$
6 $\overline{Ca}^{2+}$	0	0	1	2	−2	$\log_{10} K_3$
7 H^+	0	0	0	0	1	0

ion exchange reaction such as (16) in MICROQL, the reaction was written as the sum of two protonation-deprotonation reactions under the assumption that the *pH* remains constant. K_1 and K_2 (selectivity constants for c_1 and c_2, respectively) in Table 6 are selected so that their product yields K_{12}, the appropriate mass action selectivity coefficient.

The solution procedure for solving a binary ion exchange transport problem follows the procedure previously discussed. Solutions are first calculated for the conservative species, c_s. An estimate, c_1^*, for c_1 is calculated in the MICROQL submodel. A provisional solution, $c_{1_T}^*$, is computed using (20). An iterative procedure is followed between MICROQL and (20) until a prescribed convergence tolerance is met for c_{1_T}.

The formulation of the ternary ion exchange transport problem is similar to that for binary ion exchange except for the addition of one nonconservative transport equation and the expansion of MICROQL to include another ion exchange reaction. The general set of ternary equations can be written as

$$\frac{\partial c_i}{\partial t} + \frac{\rho \bar{c}_i}{\theta \partial t} = L(c_i) \qquad i = 1, 2, 3 \tag{21}$$

$$c_1 + \bar{c}_2 X \rightleftarrows \bar{c}_1 X + c_2 \qquad K_{12} = \bar{c}_1 c_2 / c_1 \bar{c}_2 \tag{22}$$

$$c_1 + \bar{c}_3 X \rightleftarrows \bar{c}_1 X + c_3 \qquad K_{13} = \bar{c}_1 c_3 / c_1 \bar{c}_3 \tag{23}$$

$$\bar{c}_s = \bar{c}_1 + \bar{c}_2 + \bar{c}_3 \tag{24}$$

$$c_s = c_1 + c_2 + c_3 = c_{1,0} + c_{2,0} + c_{3,0} \tag{25}$$

Addition of the three equations represented by (21) yields (19), a conservative mass balance for c_s. The original set of unknowns, (c_1, c_2, c_3), can be replaced by (c_i, c_j, c_s), where i and j equals (1,2) or (1,3) or (2,3). In keeping with the formulation and notations of *Valocchi et al.* [1981], i was set equal to 1 and j to 2. The resulting equations for c_1 and c_2 take the form of (20), where $i = 1$ and 2. MICROQL is modified to include the equilibrium chemical reactions which include the third species, c_3 and $\bar{c}_3$. The equilibrium ternary homovalent ion exchange chemistry is given in Table 7.

TABLE 7. Stoichiometry of Ternary Homovalent Ion Exchange Reactions

Species	Components c_1	c_2	c_3	$\bar{c}_s$	H^+	$\text{Log}_{10} K$
1 c_1	1	0	0	0	0	0
2 c_2	0	1	0	0	0	0
3 c_3	0	0	1	0	0	0
4 $\bar{c}_1$	1	0	0	1	−1	$\log_{10} K_1$
5 $\bar{c}_2$	0	1	0	1	−1	$\log_{10} K_2$
6 $\bar{c}_3$	0	0	1	1	−1	$\log_{10} K_3$
7 H^+	0	0	0	0	1	0

Here $(c_3)_T = c_3 + \bar{c}_3 = (c_s - c_1 - c_2) + (\bar{c}_s - \bar{c}_1 - \bar{c}_2)$.

In this case of ternary exchange there is now one conservative mass transport equation for c_s and two nonconservative equations, one for c_1 and c_2. An iterative procedure between MICROQL and (21) for c_1 and c_2 is followed until a convergence tolerance is met for both c_1 and c_2.

Simulation of Ion Exchange

Two simulations were made to demonstrate the efficacy of TRANQL and to present a direct comparison between the two modeling approaches outlined in the introduction to this paper. First, TRANQL was used to simulate the Palo Alto Baylands field project results [see *Valocchi et al.*, 1981]. Second, simulations of binary and ternary ion exchanging solutes were made.

In the first case, i.e., the field test, advanced-treated municipal effluent was directly injected into a shallow aquifer. Ion exchange of Mg^{2+} and Ca^{2+} with Na^+ is the principal chemical mechanism thought to govern transport. The equilibrium ion exchange chemical reactions considered in these simulations are given in Table 8. In this case the ion exchange reactions include heterovalent exchange. From *Valocchi et al.* [1981] the cation exchange capacity was 0.1 meq/L. The selectivity coefficients used for the exchange reaction of Mg^{2+} replacing Na^+ was $K_{21} = 1.7$ eq/L, and that for Ca^{2+} replacing Na^+ was $K_{31} = 3.0$ eq/L.

TRANQL was used to simulate the observed breakthrough of Mg^{2+} and Ca^{2+} at observation well S23, 16 m from the injection site. Radial flow was assumed, and for modeling pur-

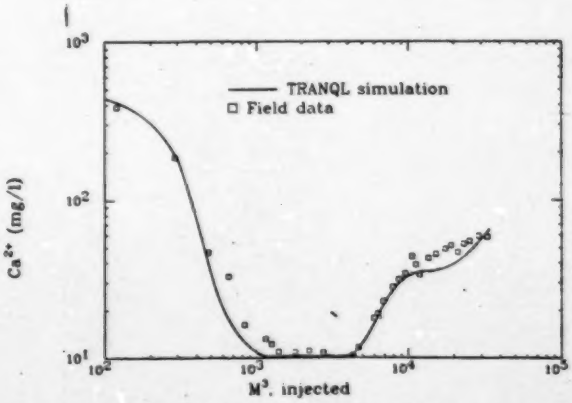


Fig. 4. Comparison of TRANQL simulation and field test [*Valocchi et al.*, 1981] for the exchanging ion Ca^{2+} at observation well S23.

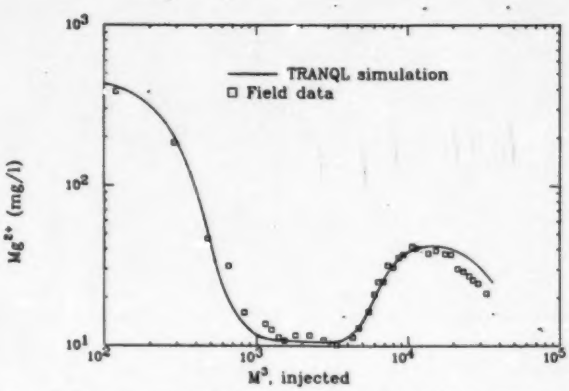


Fig. 5. Comparison of TRANQL simulation and field test [*Valocchi et al.*, 1981] for the exchanging ion Mg^{2+} at observation well S23.

poses the transport equations were modified accordingly. The simulations were run using the same input and boundary conditions, element sizes, and time steps as those of *Valocchi et al.* [1981]. The reported values of aquifer thickness (2.0 m), porosity (0.25), bulk density (1875 g/L), and dispersivities (a_l = 1.0 m and a_t = 0.1 m) were used. The injection rate of effluent water averaged approximately 21 m^2/h and had an average composition of 320 mg/L Cl^-, 216 mg/L Na^+, 12 mg/L Mg^{2+}, and 85 mg/L Ca^{2+}. The initial composition of the groundwater in the region of well S23 consisted of 5700 mg/L Cl^-, 1990 mg/L Na^+, 436 mg/L Mg^{2+}, and 444 mg/L Ca^{2+}.

Figures 4 and 5 compare the simulations of the breakthrough curves of Ca^{2+} and Mg^{2+} at well S23 to the observed field measurements. The computer predictions agree very closely with the field results and are the same as those of *Valocchi et al.* [1981].

In the second case, transport simulations of both binary and ternary ion exchanging solutes attempted to duplicate Figures 1 and 6 of *Valocchi et al.* [1981]. No graphical output is given because again, the results from TRANQL's simulations were the same as those of *Valocchi et al.* [1981].

It was expected that the numerical results of the TRANQL and Valocchi codes would be the same because the same transport code (ISOQUAD, G. F. Pinder, unpublished manuscript, 1976) and input and boundary conditions were used, the difference in the simulation lying only in the chemical submodel formulations. Whereas in TRANQL the chemical reactions are posed independently of the mass transport equations, in the work of *Valocchi et al.* [1981] the iteraction chemistry is inserted directly into the transport equations, thus requiring reformulations of the finite element matrices within each time step. Consequently, in the ion exchange simulations which are directly comparable, the execution times for TRANQL were 30% less than the execution times of the code used by *Valocchi et al.* [1981] where both codes were run on an IBM 3081 computer.

CONCLUSIONS

TRANQL is a mass transport model which has the potential to include a wide range of significant chemical equilibrium processes. In the examples presented herein, TRANQL provided for complexation of solutes in the aqueous phase, adsorption at the solid-solution interface, and ion exchange.

In the cadmium transport example the adsorption model used was the surface complexation model which includes surface ionization and complexation at the solid-solution interface. As compared to the constant charge model, the surface complexation model provides a more realistic treatment of sorbing substrates whose surface charge is not constant but a function of *p*H. Although the *p*H was held constant for reasons of simplicity, the formulation for including a variable *p*H into TRANQL is similar to the formulation required if two metals (e.g., cadmium and cobalt) compete for sorption sites and interact with the porous medium. For a second absorbing species (e.g., cobalt or H^+) another nonconservative mass balance equation similar to (7) and the inclusion of the appropriate reaction stoichiometry into MICROQL are required. TRANQL has been used to simulate the one-dimensional transport of cadmium and cobalt where both components sorbed onto the porous medium [*Cederberg*, 1985].

The constant charge sorption model was used to model binary and ternary ion exchange. The constant charge model is restricted to use on systems undergoing little or no change in *p*H. The structure of TRANQL where the equilibrium chemistry is posed independently of the mass balance equations allows for the surface complexation model and the constant charge adsorption model to be easily incorporated into TRANQL simulations.

In the case of cadmium transport, it was shown that the partitioning between the sorbed and fluid phases of the cadmium component in a multicomponent solution cannot necessarily be represented in terms of a linear isotherm involving only the aqueous species. In such solute transport cases, the use of single K_d values may lead to erroneous results. The transport of the solutes in question should be modeled with the bulk solution composition taken into account. Results from TRANQL were also sensitive to the equilibrium constants used in MICROQL. Significant sorption of cadmium was observed when the sorption equilibrium constant was at a maximum. As the sorption equilibrium constant decreased to its minimum value, sorption of cadmium in the system was less than 0.05%. Therefore the sorption equilibrium constants that result from characterizing the sorbing substrate must be determined for each multicomponent–porous medium system under consideration.

For binary and ternary ion exchanging solute systems TRANQL reproduced the hypothetical and field simulation results of *Valocchi et al.* [1981]. In the simulations of *Valocchi et al.* [1981] the finite element matrices had to be reformulated at each iteration within each time step, whereas in TRANQL the matrices never needed to be reformulated. Because the equilibrium chemical reactions are confined to and described in the MICROQL submodel, the finite element matrices need be constructed once initially and once in any TRANQL simulation. Indeed, TRANQL simulations require approximately 30% less time per case than those employing the method of Valocchi et al.

The TRANQL scheme employs a Newton-Raphson type iteration within MICROQL and a successive approximation iteration within time steps of the implicit numerical integration of the transport equation. The scheme was stable and both iterations converged for all cases reported here and in the work by *Cederberg* [1985] where a wide range of solute concentrations were used in a number of simulations. We were unable to pose any rational ion exchange or sorption cases where the method failed to converge.

Although the examples presented here were limited to one-dimensional and radial flow, TRANQL can easily be extended to simulate transport in two and three-dimensional flow re-

gimes [see *Cederberg*, 1985]. The mass balance equations are simply expanded to allow for groundwater flow and dispersion in two or three dimensions. Indeed, TRANQL has been used to simulate the two-dimensional transport of cadmium in a multicomponent solution [*Cederberg*, 1985]. The examples in this paper were presented to show how the chemical reaction submodel MICROQL can be coupled to a modified set of mass transport equations and yield good numerical results. Current research is focusing on modifying TRANQL to simulate the transport of components involved in precipitation-dissolution reactions and variable *p*H conditions. The structure and formulation of TRANQL could be extended as well to model mass transport in other systems such as streams or lakes.

Acknowledgments. This work was supported by the R. S. Kerr Environmental Laboratory of the U.S. Environmental Protection Agency under CR-808851. However, it has not been subjected to the Agency's required peer policy review and therefore does not necessarily reflect the views of the Agency, and no official endorsement should be inferred. The authors are grateful to N. B. Ball for her assistance and helpful comments.

REFERENCES

Anderson, M. P., Using models to simulate the movement of contaminants through groundwater flow systems, *CRC Crit. Rev. Environ. Control*, *9*(2), 97–156, 1979.

Bear, J., *Dynamics of Fluids in Porous Media*, 764 pp., Elsevier, New York, 1972.

Cederberg, G. A., TRANQL: A groundwater mass-transport and equilibrium chemistry model for multicomponent systems, Ph.D. dissertation, Stanford Univ., Stanford, Calif., 1985.

Charbeneau, R. J., Groundwater contaminant transport with adsorption and ion exchange chemistry: Method of characteristics for the case without dispersion, *Water Resour. Res.*, *17*(3), 705–713, 1981.

Davis, J. A., and J. O. Leckie, Surface ionization and complexation at the oxide/water interface, 2, Surface properties of amorphous iron oxyhydroxide and adsorption of metal ions, *J. Colloid Interface Sci.*, *67*(1), 90–107, 1978.

Davis, J. A., and J. O. Leckie, Surface ionization and complexation at the oxide/water interface, 3, Adsorption of Anions, *J. Colloid Interface Sci.*, *74*(1), 32–42, 1980.

Davis, J. A., R. O. James, and J. O. Leckie, Surface ionization and complexation at the oxide/water interface, 1, Computation of electrical double layer properties in simple electrolytes, *J. Colloid Interface Sci.*, *63*(3), 480–499, 1978.

Donner, H. E., Chloride as a factor in mobilities of Ni(I), Cu(II), and Cd(II) in soil, *Soil Sci. Soc. Am. J.*, *42*, 882–885, 1978.

Donner, H. E., A. Pukite, and E. Yang, Mobility through soils of certain heavy metals in geothermal brine water, *J. Environ. Qual.*, *11*(3), 339–394, 1982.

Freeze, R. A., and J. A. Cherry, *Groundwater*, Prentice-Hall, Englewood Cliffs, N. J., 1979.

Gibbs, J. W., *The Collected Works of J. W. Gibbs*, Yale University Press, New Haven, Conn., 1957.

Grove, D. B., and W. W. Wood, Prediction and field verification of subsurface-water quality and changes during artificial recharge, Lubbock, Texas, *Ground Water*, *17*(3), 250–257, 1979.

Hohl, H., and W. Stumm, Interaction of Pb^{2+} with hydrous $\gamma-Al_2O_3$, *J. Colloid Interface Sci.*, *55*(2), 281–288, 1976.

Jennings, A. A., D. J. Kirkner, and T. L. Theis, Multicomponent equilibrium chemistry in groundwater quality models, *Water Resour. Res.*, *18*(4), 1089–1096, 1982.

Leckie, J. O., M. M. Benjamin, K. Hayes, G. Kaufman, and S. Altmann, Adsorption/coprecipitation of trace elements from water with iron oxyhydroxide, *Fin. Rep. EPRI CS-1513*, Electr. Power Res. Insti., Palo Alto, Calif., 1980.

Lindstrom, F. T., and L. Boersma, A theory on the mass transport of previously distributed chemicals in a water-saturated sorbing porous medium, III, Exact solution for first order kinetic sorbtion, *Soil Sci.*, *115*(1), 5–10, 1973.

Meyers, G. E., The critical time step for finite-element solutions to two-dimensional heat-conduction transients, *J. Heat Transfer*, *100*(2), 120–127, 1978.

Miller, C. W., and L. V. Benson, Simulation of solute transport in a chemically reactive heterogeneous system: Model development and application, *Water Resour. Res.*, *19*(2), 381–391, 1983.

Pinder, G. F., and W. G. Gray, *Finite Element Simulation in Surface and Subsurface Hydrology*, Academic, New York, 1977.

Roberts, P. V., P. McCarty, and W. Roman, Direct injection of reclaimed water into an aquifer, *J. Env. Eng. Div. Am. Soc. Civ. Eng.*, *104*(EE5), 933–949, 1978.

Roberts, P. V., J. Schreiner, and G. D. Hopkins, Field study of organic water quality changes during a field study of groundwater recharge in the Palo Alto Baylands, *Water Res.*, *16*, 1025–1035, 1982.

Rubin, J., Transport of reacting solutes in porous media: Relation between mathematical nature of problem formulation and chemical nature of reactions, *Water Resour. Res.*, *19*(5), 1231–1252, 1983.

Rubin, J., and R. V. James, Dispersion-affected transport of reacting solutes in saturated porous media: Galerkin method applied to equilibrium-controlled exchange in unidirectional steady water flow, *Water Resour. Res.*, *9*(5), 1332–1356, 1973.

Schulz, H. D., and E. J. Reardon, A combined mixing cell/analytical model to describe two-dimensional reactive solute transport for unidirectional groundwater flow, *Water Resour. Res.*, *19*(2), 493–502, 1983.

Stumm, W., H. Hohl, and F. Dalang, Interaction of metal ions with hydrous oxide surfaces, *Croat. Chem. Acta*, *48*, 491–498, 1976.

Valocchi, A. J., R. L. Street, and P. V. Roberts, Transport of ion-exchanging solutes in groundwater: Chromatographic theory and field simulation, *Water Resour. Res.*, *17*(5), 1517–1527, 1981.

Westall, J., MICROQL: I, A chemical equilibrium program in BASIC, EAWAG, Swiss Fed. Inst. of Technol., Duebendorf, Switzerland, 1979.

Westall, J., and H. Hohl, A comparison of electrostatic models for the oxide/solution interface, *Adv. Colloid Interface Sci.*, *12*, 265–294, 1980.

Westall, J. C., J. L. Zachary, and F. M. M. Morel, MINEQL—A computer program for the calculations of chemical equilibrium composition of aqueous systems, *Tech. Note 18*, 91 pp., Water Qual. Lab., R. M. Parsons Lab. Water Resour. Environ. Eng., Dep. Civ. Eng., Mass. Inst. Technol., Cambridge, Mass., 1976.

G. A. Cederberg, Los Alamos National Laboratory, MS F 665, Los Alamos, NM 87544.

J. O. Leckie and R. L. Street, Environmental and Water Studies, Department of Civil Engineering, Stanford University, Stanford, CA 94305.

(Received July 3, 1984;
revised March 7, 1985;
accepted March 19, 1985.)

NOTICE

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

This article documents research that was conducted under the auspices of the U.S. Environmental Protection Agency (USEPA). As an arm of the government, the USEPA has a paid up, non-exclusive, irrevocable, worldwide license to reproduce, prepare derivative works, and distributs to the public all of the material contained herein, and to grant others acting on its behalf the right to do so. The USEPA grants to the National Technical Information Service, Department of Commerce, the right to act as its agent in the distribution of this material.